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The Influence of Thermal Column History on the Retention Behaviour in Inverse Gaschromatography

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Summary

The influence of thermal history of the stationary phase in inverse gas chromatography has been studied, using polystyrene and solvents of very different solubility behaviour. While no differences in retention volumes are observable well above T_g,strongly deviating retention values are determined around and below T_g. Changes in retention behaviour can be correlated to a change in surface to volume ratio of the polymer and its influence on combined surface and bulk retention mechanism. Examplified by the system polystyrene/nitromethane the results give evidence for a different solution mechanism above and below T_g of the polymer.

Introduction

Usually conditioning of a freshly packed chromatographic column is carried out at or above the highest temperature of measurement for a period of 24 hours. This treatment primarily is designed to purify the polymeric layer from residual solvent used in the coating procedure. Investigations of coatings of the inert support material with two seperate layers of different polymers[1,2) required a conditioning procedure at rather low temperatures, in order to prevent a mixing of the two polymeric layers. In the course of this investigations it was observed, that the temperature of the conditioning step seemed to be of influence on the retention behaviour of some solutes. It is the purpose of this paper to report on the results of a systematic investigation of this operational parameter on retention data determined on polystyrene columns.

Experimental

Retention data were measured on a Siemens L 400 gas chromatograph, equipped with a flame ionisation detector. Polystyrene 158 K of BASF ($\overline{M}_n$: 144 000; T_g≈100 °C) was studied as stationary phase using Chromosorb WAWDMCS, 45 - 60 mesh,(Johns-Manville-Products) as inert support. The polymer loading was 10 % per weight basis and benzene was used as solvent in the coating process. The n-alkanes C_8 - C_{11}, benzene and nitromethane (NM) were used as solutes. 0.02 ml of the vapour phase of the solutes were injected together with the same amount of methane (inert gas).

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A list of the prepared columns and of the series of measurements is given in table I.

Table I: Thermal Treatment of the Prepared Columns

No.	Loading (%)	Loading (g)	Conditioning Temperature (^oC)		Measurement Temperature Programm	
Ia	10.4	0.5049	40	(24h)	upwards	(40-180 ^oC)
Ib	10.4	0.5049	40	(24h)	downwards	(180- 40 ^oC)
IIa	10.3	0.4908	101	(24h)	upwards	(40-180 ^oC)
IIb	10.3	0.4908	101	(24h)	downwards	(180- 40 ^oC)
IIIa	10.2	0.4980	180	(24h)	upwards	(40-180 ^oC)
IIIb	10.2	0.4980	180	(24h)	downwards	(180- 40 ^oC)

The measurements were made in the temperature range 40 - 180 ^oC (curves a) respectively 180 - 40 ^oC (curves b) in steps of 10 ^oC at a standard flow rate of the carrier gas of 35 ml per minute. At some temperatures (70, 120 and 170 ^oC) additional experiments were carried out at variable flow rates. The results were plotted in log V_g^o versus 1/T-diagrams, where the V_g^o values were obtained by the well known equation

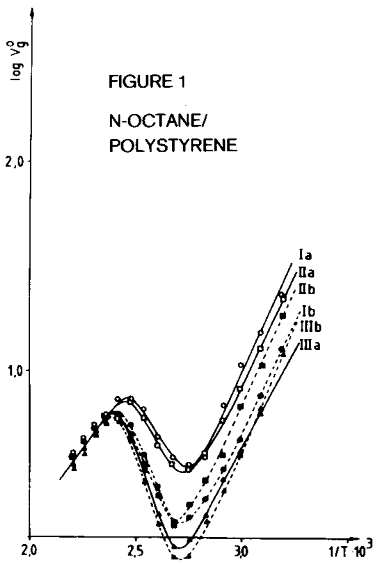
$$V_g^o = \frac{t_r \cdot F}{W} \; \frac{273.16}{T_f} \; \frac{p_o - p_w}{p_o} \; \frac{3}{2} \; \frac{(p_i/p_o)^2 - 1}{(p_i/p_o)^3 - 1} \qquad (1)$$

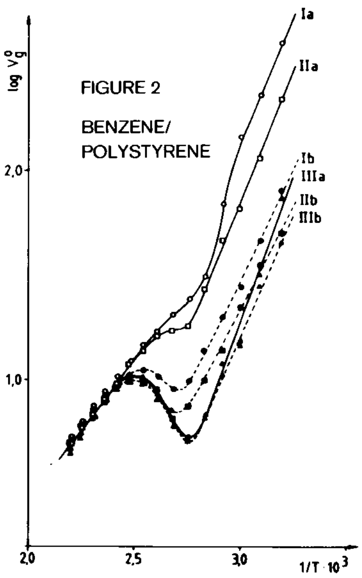
V_g^o specific net retention volume, t_r net retention time, F flow rate of the carrier gas, W weight of the stationary phase (polymer), T_f temperature of the flowmeter, p_o atmospheric pressure, p_w vapour pressure of water at T_f, p_i inlet pressure of the column.

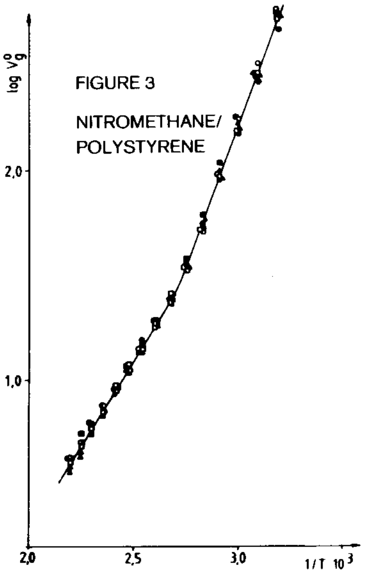
The results are shown in the figures 1 - 3.

Results and Discussion

The figures 1 and 2 show a substantial dependence of the V_g^o vs 1/T curves on the thermal history of the column, which is determined by the conditioning temperature and by the temperature/time programm of the respective experimental series. In figure 3 however the influence of column history is negligible.







Figures 1-3: Dependence of the specific retention volume of n-octane, benzene, and nitromethane on the reciprocal absolute temperature for different thermal treatment (conditioning) temperature.
Sequence of measurement: *a*: 40-180°C (○ □ △), *b*: 180-40°C (● ■ ▲)
conditioning temperature: I: 40°C (● ○), II: 101°C (□ ■), III: 180°C (△ ▲)

The most important feature in Fig. 1 and 2 is the development or enhancement of the z-type retention diagram with increasing residence time of the column at 180 °C. Now it is well known that the z-shape is related to a transition of surface to bulk retention mechanism in the vicinity of T_g of the polymeric stationary phase. Since the bulk retention values, determined at temperatures well above T_g ($T > 140$ °C) for all solutes are practically identical and independent of pretreatment of the column, the different retention volumes at lower temperatures are clearly caused by a change in available surface area (A), detectable in those cases where surface (adsorption) retention plays a significant role. This is quantified by equation (3) (if contributions originating from solute retention at the support surface are negligible). The net retention volume can be written as

$$V_n = K_A \cdot A + K_B \cdot m \qquad (2)$$

where K_A and K_B are the partition coefficients due to adsorption and absorption; A is the available surface area of the polymeric coating and m is the mass of the polymeric coating

and then the specific retention volume V_g^o is

$$V_g^o = \frac{V_n}{m} = K_A \cdot \frac{A}{m} + K_B \qquad (3)$$

Figure 1 shows the retention behaviour of an n-alkane, C_8, which is a nonsolvent for polystyrene. Whilst above T_g ($T > 140$ °C) this solute is dissolved in the polymeric phase (bulk absorption mechanism, i.e., $K_A \cdot A/m \ll K_B$), well below T_g only surface adsorption can be assumed ($K_B \ll K_A \cdot A/m$).

The systematic shift in V_g^o has to be interpreted as an effect of a decreasing surface area - which at constant loading is identical to a decreasing surface to volume (mass) ratio - with prolonged column treatment at 180 °C. The change in V_g^o furthermore gives a quantitative estimate of the surface area decrease. Assuming that surface adsorption is the only retention mechanism, the ratio of two V_g^o values is given by

$$\frac{V_{g_1}^o}{V_{g_2}^o} = \frac{K_A \cdot \frac{A_1}{m}}{K_A \frac{A_2}{m}} = \frac{A_1}{A_2} \qquad (4)$$

The V_g^o values (extrapolated to zero flow rate) at a measuring temperature of 70 °C for the curves Ia and IIIb for C_8 are $V_g^o = 7.925$ and $V_g^o = 2.825$, the ratio of surface areas is therefore 2.8.

This can be interpreted as follows: The polymer structure originating from the solvent evaporation process can be considered to be rather loose and rich in surface, a structure which is maintained as long as $T < T_g$. At elevated temperatures ($T > T_g$) and increasing time,surface tension can become effective which leads to a minimisation of the surface area. This interpretation corresponds to the experiments of BRAUN and GUILLET[3)], where the factor (A/m) has been changed by variation of m.

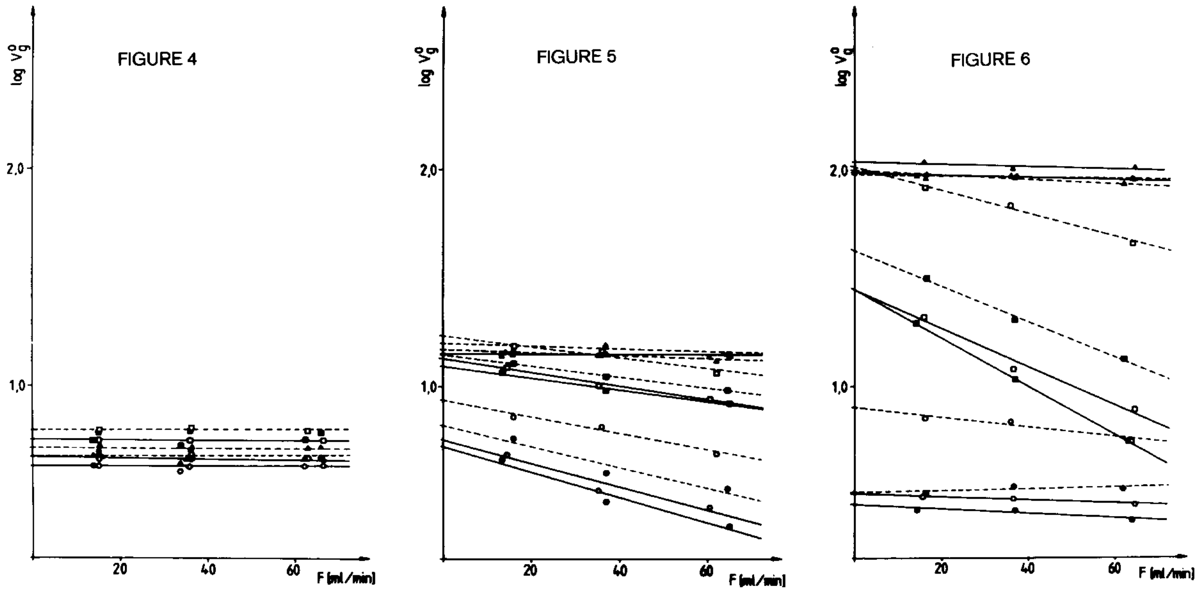
Another limiting case is obviously examplified by the solute nitromethane, see Fig. 3. The fact that - not only above, but also below T_g - V_g^o is independent on thermal history is only understandable assuming bulk absorption in both regions, so that the first term on the right hand side of equation (3) is negligible ($K_A \cdot A/m \ll K_B$). We will come back to this case later.

The solute benzene, a good solvent for polystyrene, shows the mostdrastic change in V_g^o with thermal column history (see Fig.2). In this case at $T < 140$ °C both terms on the right hand side of eq. (3) have to be of comparable order of magnitude. Due to measuring under non equilibrium conditions (see Fig. 4 and 5)the availability of the polymer mass for absorption is of great influence. In case of a very thin polymeric layer, as is directly obtained from the coating procedure, the surface area is very large and practically the whole polymer mass is available for interaction. This results in rather big contributions of both surface adsorption and bulk absorption. The shape of the curve is very straight and similar to that of nitromethane. In case of thicker layers the polymer mass available for bulk absorption becomes smaller. Simultaneously the surface area is decreasing.This results in smaller V_g^o values. With increasing thermal treatment the shape of the curve therefore changes to a significant z-shape (column IIIb).

Additional evidence to support the mechanistic interpretations given above can be obtained from studies on variation of carrier gas flow rate and its effect on V_g^o (Figs. 4-6). In an equilibrium situation, i.e., where only one retention mechanism(i.e., adsorption or absorption) is dominating, V_g^o values are generally observed to be flow rate independent. Superposition of surface adsorption and bulk absorption in a mixed retention situation generally is realized in a non equilibrium case, which gives rise to a decrease in V_g^o with increasing flow rate (due to a decreasing interaction with the bulk phase).

As shown in Fig.4, well above T_g ($T > 140$ °C) V_g^o values of all solutes can be shown to be flow rate independent, in accordance with the statement about bulk absorption given above. In the transition region ($T = 120$ °C), n-octane as well as benzene show a flow rate dependence, but nitromethane does not. Below T_g ($T = 70$ °C) flow rate invariant V_g^o values are obtained for n-octane (due to predominant surface retention) and nitromethane (bulk retention) while benzene shows a strong flow rate dependence.

Summarizing these results, it is generally evident that column history can have a significant influence on retention data in



Figures 4-6: Flow rate dependence of the specific retention volume at various conditioning temperatures.
Conditioning temperature: - - - 40°C, —— 180°C
temperature sequence: 40-180°C (○ □ △), 180-40°C (● ■ ▲)
solutes: ○● n-octane, □■ benzene, △▲ nitromethane
measuring temperature: Fig. 4: 170°C, Fig. 5: 120°C, Fig. 6: 70°C

inverse gas chromatography. Furthermore definitely more than one type of solute has to be investigated in order to prove stable column conditions and variation of carrier gas flow rate is an important additional tool to get insight into the mechanism of solute retention. A more fundamental problem however is touched by the findings on the nitromethane/polystyrene system.

Usually a change in the slope of the V_g^o vs 1/T curve at T_g is assigned to a change in retention behaviour from an absorption to adsorption mechanism, and from the slopes of such diagrams the corresponding enthalpies ΔH_S and ΔH_{ad} are calculated. As has been proved by other experiments too[2] nitromethane/polystyrene interaction follows an equilibrium bulk absorption mechanism not only above but also below T_g. A change in the V_g^o vs 1/T slope therefore indicates different heats of solution for a given solute in the same polymer depending on the structure of the polymeric matrix. Inverse gas chromatography seems especially suitable for further studies of such phenomena[4].

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